

Patent Forms

Patent Application and Drawings

Zabetakis, Bureau of Mines

US Patent 5060291, O'Connell

Solid State Tech, Arno

US Patent 5518528

J. Phys Chem Tamaru

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A Method for Safe Handling of Unstable Hydride Gases

U. S. Patent Application of:

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1 TITLE OF THE INVENTION  
23 A Method for Safe Handling of Unstable Hydride Gases  
45 BACKGROUND OF THE INVENTION  
6

7 This invention relates generally to the field of safe handling of chemicals, and  
8 more particularly to a method and apparatus for preventing fire and explosions in the  
9 production, purification and transportation of unstable hydrides by subdividing the  
10 enclosure containing the hydride and providing localized heat storage and heat transfer  
11 means to remove heat from an incipient fire or explosion so as to prevent propagation  
12 of the aforesaid fire or explosion.

13  
14 The invention relates to a method for preventing the occurrence of a fire or  
15 explosion in an enclosure. The term " enclosure" as used herein describes a space  
16 having a boundary that substantially encloses the perimeter of the space such as a  
17 storage tank, a cylinder, a duct, a cavity, or a vessel, which may be at any pressure.  
18 The enclosure has one or more openings to permit the ingress and egress of materials  
19 and said openings may be sealed by devices such as flanges or valves and may be  
20 connected in series with other enclosures.

21 The problem of fire and explosions in enclosed spaces has been a serious issue  
22 for many years. It was recognized that these explosions required a source of ignition  
23 and also a sufficient amount of the flammable gas and air. Thus the "Lower Explosive  
24 Limit" of a particular gas is defined as the minimum amount of the gas mixed with air at  
25 room temperature and pressure, which would explode in the presence of a source of

1 ignition and is referred to as "LEL". The "Upper Explosive Limit" of a particular gas is  
2 defined as the maximum amount of the gas mixed with air at room temperature and  
3 pressure, which would explode in the presence of a source of ignition and is referred to  
4 as "UEL". Thus it was recognized that it was possible to have a safe mixture of  
5 potentially explosive gas with air providing the concentration of the gas was either below  
6 the LEL or above the UEL. The LEL and UEL provide useful concepts for room  
7 temperature and pressure situations in air and can be modified to account for  
8 temperature pressure and the presence of other gases. The addition of a gas to  
9 another gas is termed "diluting" and the added gas is the "diluent". Zabetakis provides  
10 in Bureau of Mines Bulletin 627 flammability, data for more than 200 combustible gases  
11 and vapors and graphs and empirical rules that can be used for adjusting the LEL and  
12 UEL for gases under different conditions from the standard room temperature and  
13 dilution with air. It is thus possible to adjust the flammability range. The bulletin also  
14 notes that for gases such as hydrazine, which can burn in the absence of an oxidizer,  
15 the UEL is 100% but it is possible to add stable diluents that will render the mixture  
16 nonflammable. The effect of tube diameter on the decomposition of pure acetylene is  
17 shown in Fig 61 of the Bulletin and shows the inverse log-log relationship of pressure  
18 and diameter.

19 It was also recognized that fire and explosions were related phenomenon with  
20 explosions being extremely rapid fires. Thus since it was well known that water and  
21 other chemicals would put out fires, the idea of suppressing explosions with water or  
22 other chemicals has been studied and can be effective providing the explosion is  
23 detected and suppressed before it builds up to destructive power.

24 There are two types of technology for safe handling of potentially hazardous  
25 gases in enclosures, the prevention approach and the suppression approach. In the

1 prevention approach the technology attempts to prevent a fire or explosion from starting  
2 by removing the source of ignition or by operating in a non-flammable regime.

3 Removing the source of ignition may mean use of intrinsically safe, low voltage,  
4 sensors, protecting against static discharge and external insulation to protect against  
5 fire and operating below the auto ignition temperature, the temperature at which a  
6 material explodes without a source of ignition. The main advantage of the removal of a  
7 source of ignition is that it is relatively low cost; its major disadvantage is that there may  
8 be an unexpected source of ignition in which case there is no protection. The  
9 unexpected sources of ignition can be a catalytic reaction with the wall of the enclosure  
10 or with corrosion products on the wall, such reactions typically form hot spots that slowly  
11 accumulate heat until a fire or explosion can propagate.

12 One common example of operating in a non-flammable regime is the use of nitrogen  
13 "blankets" over flammable liquids stored in atmospheric pressure tanks to prevent fires.  
14 This is an example of dilution with nitrogen of a flammable vapor and air mixture.  
15 Sufficient nitrogen is provided to raise the LEL of the mixture so that the mixture is not  
16 flammable at the operating conditions of the tank. For sealed gas cylinders, certain  
17 gases that decompose without an oxidizer, i.e. an upper UEL of 100%, are shipped in a  
18 diluted form such that they are non-flammable. Alternatively they may be shipped or  
19 used at reduced pressure since reducing the pressure has been shown to reduce the  
20 risk of deflagration, as shown in Fig 61 of Zabetakis for Acetylene. They may also only  
21 be shipped in small cylinders since lowering the diameter lowers the risk.

22 The advantage of operating in the nonflammable regime is that it is a passive  
23 system and will prevent fires and explosions within the conditions it is designed for.  
24 However the lack of purity is particularly a problem during production and purification of  
25 the flammable materials, particularly materials, which are flammable without an oxidizer.

1 The standard purification techniques of distillation and membrane separation can be  
2 carried out in the substantial absence of air fairly readily for materials that are stable in  
3 the absence of an oxidant because it is possible to operate above the UEL. However  
4 for materials, which have a UEL of 100% because they can decompose in the absence  
5 of an oxidant, there is no safe region for distillation of the pure material. Use of a diluent  
6 gas increases the capital and operating cost of the purification material because it must  
7 be bigger and process more material as well as recycle the diluent. Another variation  
8 has been to absorb the gas on a solid sorbent as in U.S. Patent 5,518,528. This  
9 reduces the pressure in the headspace of the enclosure and stores the majority of the  
10 gas as an adsorbed species, which is attached to the sorbent by physical or chemical  
11 forces. To desorb the gas from the apparatus it is necessary to reduce pressure, add  
12 heat or a combination of the two. As noted in the above patent the sorbent can promote  
13 decomposition of the stored gas and special precautions are required to avoid this  
14 problem. Adsorption-desorption systems are more complicated for the end user in  
15 comparison to a gas cylinder thus they tend to be considerably more expensive to buy  
16 and operate. This technique is also not applicable to such standard separation  
17 techniques as distillation or membrane separation.

18 The suppression type of technology relies on the detection of incipient fire or  
19 explosion and then rapidly suppressing the event.

20 US Patent 5069291 describes a system of detecting the incipient pressure rise of  
21 an explosion and suppressing that explosion by spraying hot pressurized water into the  
22 enclosure. The patent claims that the explosion must be detected and suppressed  
23 within 10-200 milliseconds and discusses competing technology using chemicals such  
24 as Halon 1011 (chlorobromoethane) and MAP (monoammonium phosphate). The use  
25

1 of Halon is being restricted because of concerns about ozone depletion and the use of  
2 any suppressant will contaminate the enclosure.

3  
4       Suppression type systems rely on rapid detection and on the careful design of  
5 the flow of the suppressant to the site of the fire or incipient explosion. Suppression of  
6 explosions must be much faster than fires and so the detection and activation of the  
7 suppressant discharge is advantageously combined as in US Patent 5069291. The  
8 prior art for direct suppression of fire or explosions is an active system that requires fast  
9 detection and response to inject a quenching chemical into the enclosure that may fail  
10 or be too slow to prevent the explosion. It is well known to engineers that systems that  
11 are not in regular use may not work when needed because of lack of maintenance or an  
12 undetected fault. Thus it is normally required to have some routine testing to ensure the  
13 equipment still works, which adds cost and may require decontamination of the  
14 enclosure after testing. After each suppression of fire or explosion the enclosure is also  
15 contaminated with the suppressant materials and some initial products of the reaction.  
16 With the increased emphasis on safety the avoidance of flammability approach has  
17 become the most common solution because it is essentially a passive system and will  
18 prevent fires and explosions within the conditions it is designed for although if the  
19 temperature and or the pressure rise above design conditions the gas may become  
20 flammable. The major problems are that the diluent gas must be provided and in the  
21 case of transportable containers must be also shipped which adds additional cost for  
22 the larger container. The larger container also occupies more space during production,  
23 distribution and use. Use of lower pressure containers also increases the size of the  
24 container and restricting the size of the container increases the cost because it is not  
25 possible to obtain economies of scale. A further problem is that the mixture of gases is

1 by definition no longer pure, which is only a minor problem for flammable liquids, since  
2 the vapor and diluent mix can be discarded but is a big problem for flammable gases

3 The lack of purity is particularly a problem during production and purification of  
4 materials which have a 100% UEL because there is no safe region for distillation of the  
5 pure material in contrast to the ease with which standard purification techniques of  
6 distillation and membrane separation can be carried out safely for materials which have  
7 a UEL less than 100% simply by operating above the UEL. The option of using a  
8 diluent increases the capital and operating cost of the purification material because the  
9 separation equipment must be bigger and process more material. Using lower pressure  
10 and temperature decreases the risks but also increases the costs as the equipment  
11 must be larger and refrigeration equipment increases in cost as the temperature  
12 decreases.

13 Many of the gases with 100% UEL are unstable hydride gases such as hydrazine,  
14 acetylene, silane and germane. A hydride gas is a gas containing hydrogen. Unstable  
15 gaseous hydrides are gaseous compounds containing hydrogen that have a positive  
16 heat of formation. Examples of such gases are found in the compounds of hydrogen  
17 with elements from the 4th, 5<sup>th</sup> and 6<sup>th</sup> column of the periodic table. The term heat of  
18 formation refers to the heat required to form a given compound from the elements of  
19 which it is comprised. A negative heat of formation means that heat is given out when  
20 the two elements are combined, as an example the formation of water from hydrogen  
21 and oxygen provides a large release of heat and conversely the production of the  
22 elements from the compound requires the addition of energy. A positive heat of  
23 formation means that heat must be added to form the compound from its elements, as  
24 an example Silane,  $\text{SiH}_4$ , requires the addition of heat for its formation and generates  
25 heat when it decomposes to form the elements. Such gases are very useful in the



1 semiconductor industry for the deposition of pure metals, particularly semiconductors  
2 such as silicon and germanium, since they can be produced in a highly purified form by  
3 techniques such as distillation. A major disadvantage of such gases is that the  
4 decomposition can occur during production of the gases particularly when the gases are  
5 condensed under pressure to form liquids suitable for distillation. The decomposition  
6 causes a rise in temperature and pressure from the heat release and the production of  
7 hydrogen gas. The temperature rise can weaken the construction materials of the  
8 container of the gas, which in combination with the rapid pressure rise can result in  
9 rupture of the container. The temperature and pressure rise are proportional to the heat  
10 of formation. One method for assessing the risk of such decompositions is to calculate  
11 the adiabatic temperature and pressure that would occur during decomposition in the  
12 absence of any heat loss from the gas and design the container so that these conditions  
13 can be withstood. , See Arno. This latter assumption is fairly valid for the extremely  
14 rapid explosive reactions, which are the main concern since heat exchange is much  
15 slower than the reaction. These calculations use the known heat of formation to  
16 calculate the adiabatic heat release, and then use the known heat capacities of the  
17 reaction products produced to calculate the peak temperature produced when all the  
18 released heat is used to heat the produced elements. This temperature can be used to  
19 calculate the pressure rise due to temperature increase. There is also an increase in the  
20 number of gas moles, which contributes further to the pressure rise. The multiplication  
21 of these two effects gives the total pressure ratio, which is defined as the final pressure  
22 over the initial pressure. The table below gives the calculations based on a starting  
23 temperature of 25°C for typical hydrides.

#### 24 EXAMPLE 1 ACETYLENE

25

There are two decomposition routes since methane is more stable than its elements:



Example 2 Germane

Germane has only one decomposition route



Table 1 Peak temperature & pressure for selected hydride gas decomposition

Name	Formula	Heat of Formation kcal/mole	Moles gas/mole	Temp. C	Press. ratio
Acetylene	$\text{C}_2\text{H}_2$	54.2	.5-1	2902-3278	6-10.5 *
Propadiene	$\text{C}_3\text{H}_4$	45.9	1-2	1584-2159	8.2-12.5
Methylacetylene	$\text{C}_3\text{H}_4$	38.97	1-2	1376-1975	7.5-11
1-3, butadiene	$\text{C}_4\text{H}_6$	26.1	1.5-3	803-1374	8.29-10.8
Ethylene	$\text{C}_2\text{H}_4$	12.5	1-2	606-1427	5.7-5.9
Propylene	$\text{C}_3\text{H}_6$	4.9	1.5-3.0	195-1091	4.7-6.86
Hydrazine	$\text{N}_2\text{H}_4$	22.75	3	1066	13.5
Silane	$\text{SiH}_4$	8.2	2	448	4.8
Disilane	$\text{Si}_2\text{H}_6$	19.192	3	616	5.97
Germane	$\text{GeH}_4$	21.7	2	937	8.12
Digermane	$\text{Ge}_2\text{H}_6$	38.8	3	937	12.18
Stannane	$\text{SnH}_4$	38.9	2	1741	13.5
Arsine	$\text{AsH}_3$	14.63	1.5	817	5.5
Stibine	$\text{SbH}_3$	34.68	1.5	1660	9.72
Bismuthine	$\text{BiH}_3$	43.0	1.5	2259	12.75

Hydrogen Selenide	H <sub>2</sub> Se	7.17	1	425	4.68
Hydrogen Telluride	H <sub>2</sub> Te	23.8	1	1352	5.45

\*The experimental measurement for deflagration in acetylene vapor is 11 times the initial pressure, which agrees with these calculations.

Another approach is to dilute the hydride with hydrogen and the appropriate conditions for this can be determined experimentally, see Arno, or by a similar calculation to that used in the prior examples except by adding a diluent which must also be heated and thus reduces the peak temperature. The problem then becomes what is a "safe" peak temperature. One approach has been to match the peak conditions of 100% silane as traditionally silane has been purified and stored with standard techniques. Thus "safe" can be the concentration of the pure material in hydrogen which would have a similar peak temperature and pressure rise to that of silane.

Example 1 Disilane at 40% by volume in hydrogen

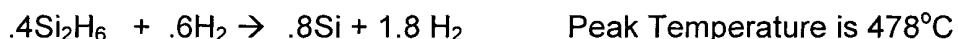


Table 2 Examples of Dilution requirements to match 100% silane

Name	Formula	Max %	gas moles ratio (out/in)	Temp. C	Pressure ratio
Disilane	Si <sub>2</sub> H <sub>6</sub>	40	1.8	478	4.5
Germane	GeH <sub>4</sub>	20	1.2	481	3
Digermane	Ge <sub>2</sub> H <sub>6</sub>	10	1.33	434	3.15
Stannane	SnH <sub>4</sub>	10	1.33	473	3.33
Arsine	AsH <sub>3</sub>	30	1.15	470	2.5

Thus the additional heat required to heat the hydrogen diluent reduces the peak temperature and the pressure ratio to that similar to silane. Note that Arno quotes an

1 upper concentration of 20% for germane which corresponds well to this "silane  
2 matching criteria as can be seen from the table above. Applying these same safety  
3 considerations to the design of the separation systems will increase the cost compared  
4 to standard practice. However the assumptions of comparability to silane are not as  
5 valid as believed because silane has a higher temperature of decomposition, 340°C  
6 than other hydrides such as germane, 278°C or acetylene, 280°C. Silane preferably  
7 reacts in the gas or homogeneous phase while germane and acetylene more easily  
8 react on the surface. Surface dependent decomposition is affected by the surface and  
9 different surfaces can initiate decomposition at lower temperatures. For example  
10 Tamaru discusses the increase in reaction rate caused by the presence of trace  
11 amounts of oxygen on the germanium surface. The lack of understanding of the  
12 underlying mechanisms and the disadvantages of using a gas as a diluent lead to a  
13 desire to minimize the use of diluent and to use experimental testing as the main way of  
14 establishing safety as discussed by Arno. Such tests are expensive and are carried out  
15 with carefully prepared and frequently small containers, see Arno, which tends to mean  
16 that too few tests are carried out to pick up surface catalysis problems resulting from a  
17 low probability inadvertent contamination event and that the inherent additional safety  
18 caused by the diluent effect of the small diameter container is ignored. Thus on scale up  
19 to production sizes, quantities and conditions the safety is significantly reduced. Since  
20 the matching of silane conditions is not as safe as perceived by current practitioners it is  
21 desirable to design the system for a given hydride based on the decomposition  
22 properties of that hydride as in the present invention.  
23  
24  
25

1 BRIEF SUMMARY OF THE INVENTION  
2

3 A primary object of the invention is to safely handle unstable hydride gases

4 Another object of the invention is to passively suppress incipient fires and  
5 explosions in such gases

6 Another object of the invention is to allow safe transport of unstable hydride  
7 gases.

8 A further object of the invention is to permit safe separation of unstable hydride  
9 gases.

10 Yet another object of the invention is to permit safe production of pure unstable  
11 hydride gases.

12 Still yet another object of the invention is to permit safe distillation of unstable  
13 hydride gases.

14 Another object is to require no changes to the standard operating procedure for  
15 the storage or processing enclosure/s.

16 In accordance with a preferred embodiment of the present invention, a method  
17 for safe handling of unstable hydride gases comprises an enclosure with one or more  
18 openings, a partitioning means to divide the said enclosure into smaller volumes, one  
19 or more connecting passageways between each smaller volume and an opening to the  
20 enclosure, a means to store heat within the said enclosure, a heat transfer means from  
21 every smaller volume to the means to store heat, and sizing the partitions, the heat  
22 sinks and the heat transfer means so as to prevent the temperature of the gas or gases  
23 in any of the smaller spaces from reaching the minimum temperature needed to cause  
24 ignition or decomposition of the gas or gases in an adjoining space. The method can  
25 be readily applied to the production, purification and shipping of highly pure unstable

1 hydrides by use of a reusable solid diluent to subdivide the tanks, pipes, distillation  
2 columns and cylinders into smaller enclosures and provide heat storage to prevent  
3 propagation of fires and explosions. The solid diluent can easily be fabricated from  
4 hollow tubes, wire mesh or waste materials such as turnings, and can be reused. The  
5 solid diluent material can be any solid except materials known to significantly adsorb,  
6 react with or cause the catalytic decomposition of the hydride which is to be stored in  
7 the enclosure. The use of materials that briefly react with the hydride then form a  
8 passive coating is permitted as it is a standard passivation technique for enclosures.  
9 For certain applications it may be desirable to have a non-reusable solid diluent. Such  
10 diluents utilize a phase change such as melting or vaporization or chemical reactions to  
11 absorb more heat for a given amount of diluent than is possible when the heat is  
12 absorbed only in raising the temperature of the diluent. Such applications would need  
13 provision to provide a warning that an incipient event had occurred.

14 Other objects and advantages will become apparent from the following  
15 descriptions, taken in connection with the accompanying drawings, wherein, by way of  
16 illustration and example, an embodiment of the present invention is disclosed.

#### 19 BRIEF DESCRIPTION OF THE SEVERAL DRAWINGS

21 The drawings constitute a part of this specification and include exemplary  
22 embodiments to the invention, which may be embodied in various forms. It is to be  
23 understood that in some instances various aspects of the invention may be shown  
24 exaggerated or enlarged to facilitate an understanding of the invention.

1        Figure 1 is a graph illustrating that the peak temperature obtained when a  
2        quantity of germane explodes or burns can be reduced by addition of a diluent and that  
3        on a molar basis the effect is similar for the prior art gaseous hydrogen diluent and  
4        solid aluminum diluent and more effective for silica,  $\text{SiO}_2$

5        Figure 1b is a graph illustrating that a far greater weight of aluminum and silica  
6        is required, for the same temperature reduction effect, compared to hydrogen.

7        Figure 1c is a graph illustrating that the volume percent of the enclosure, for the  
8        same temperature effect, occupied by the diluent is much less for the solid aluminum  
9        and silica diluents than for the gaseous hydrogen and that a higher pressure enclosure  
10       requires a proportionately greater solid volume.

11       Figure 2a is a schematic representation of the invention as applied to a gas  
12       cylinder.

13       Figure 2b is a schematic representation of the invention as applied to a  
14       horizontal pipe.

15       Figure 3a is a schematic representation of the prior art packed distillation  
16       column showing open areas where explosions of fires can occur.

17       Figure 3b is a schematic representation of the invention as applied to the prior  
18       art packed distillation column showing that the open areas where explosions of fires  
19       can occur have been rendered safe by filling with a solid diluent.

20       Figure 4a is a side view of a piece of solid diluent made by cutting a hollow tube  
21       into lengths.

22       Figure 4b is a cross sectional view of a loosely packed arrangement of hollow  
23       tubes.

24       Figure 4c is a cross sectional view of a tightly packed arrangement of hollow  
25       tubes.

1 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS  
2

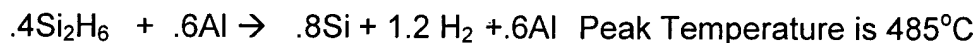
3 Detailed descriptions of the preferred embodiments are provided herein. It is to  
4 be understood, however, that the present invention may be embodied in various forms.  
5 Various aspects of the invention may be inverted, or changed in reference to specific  
6 part shape and detail, part location, or part composition. Therefore, specific details  
7 disclosed herein are not to be interpreted as limiting, but rather as a basis for the  
8 claims and as a representative basis for teaching one skilled in the art to employ the  
9 present invention in virtually any appropriately detailed system, structure or manner.

10 Turning first to Fig 1a there is shown the prior art of dilution of germane with  
11 gaseous hydrogen to reduce the peak temperature and the comparison of it to the  
12 present invention of the use of solid aluminum or silicon dioxide, silica, as the diluent. It  
13 can be seen that the effect on a molar basis is essentially the same for hydrogen and  
14 aluminum with silica being considerably better. Silica is the prime ingredient in sand  
15 and in glass thus this applies to a wide range of diluents. Figure 1b shows the same  
16 reduction in peak temperature for hydrogen, silica and aluminum diluents compared on  
17 a weight basis rather than a molar basis. The weight of aluminum or silica required for  
18 a given reduction in peak temperature is much higher than for hydrogen because of the  
19 low molecular weight of hydrogen. Figure 1c shows the same reduction in peak  
20 temperature for hydrogen and aluminum diluents compared on a volume basis rather  
21 than a molar basis. The volume of aluminum or silica required for a given reduction in  
22 peak temperature is much lower than for hydrogen as the molal volume of a solid is  
23 much lower than the molal volume of a gas. This graph also shows that there is no  
24 effect of pressure on the required hydrogen volume but the required aluminum or silica  
25 volume is directly proportional to the pressure.



1 This is a result of the fact that the molal volume of germane and hydrogen are  
2 both dependent on pressure whereas the molal volume of a solid like aluminum or silica  
3 is independent of pressure. Hence as the number of moles of germane increase in a  
4 given volume because of the increase in pressure the germane to hydrogen molal ratio  
5 remains the same but the molar germane to aluminum ratio decreases for a fixed  
6 volume of aluminum. However it can be seen that the volume of aluminum or silica  
7 required is much less than that of hydrogen even at 10 atmospheres pressure. Thus it  
8 is feasible to provide the equivalent heat storage capacity at a much lower volume with  
9 aluminum or silica than with hydrogen. Because of the inherent difference in density  
10 between gases and solids this will be true for most comparisons of gas and solid  
11 diluent. Fig 1d shows the effect of using the much more energetic acetylene. The  
12 temperatures obtained are higher and more diluent must be used to bring the peak  
13 temperature down below the decomposition temperature. It is still feasible to use 250-  
14 psig gases with about 33% diluent. From Fig 61 of Zabetakis it can be seen that the  
15 "tube diameter" needs to be less than 0.02 inches to prevent propagation at this  
16 pressure. This is 0.5 mm or 500 microns. Thus a suitable low cost diluent could be  
17 sand. The void fraction of sand is typically about 0.35, which means a diluent factor of  
18 0.65 or 65%. The average particle size would be 1000-1500 microns. Such a design  
19 would have a safety factor of about 2. The fixed volume of the solid diluent has no effect  
20 on the volumetric change caused by the pure reaction in comparison to dilution with  
21 hydrogen as shown in Table2

22 Example 1 Disilane at 40% molar with aluminum



Assuming the cylinder is at 0.4 atmospheres initially then the final pressure is  $0.4 \times 7.63$  atm = 3 atm compared to a final pressure of 4.5 atm for the hydrogen dilution cylinder at 1 atm initially.

Table 3

Name	Formula	Mol %	gas moles ratio (out/in)	Temp. C	Pressure ratio
Disilane	$\text{Si}_2\text{H}_6$	40	3	485	7.63
Germane	$\text{GeH}_4$	20	2	497.2	5.16
Digermane	$\text{Ge}_2\text{H}_6$	10	3	452	7.3
Stannane	$\text{SnH}_4$	10	2	492.8	5.13
Arsine	$\text{AsH}_3$	30	1.5	483.7	3.8

Thus the additional heat required to heat the solid diluent reduces the peak temperature in a manner similar to dilution with hydrogen and requires much less volume but does not reduce the pressure ratio as much. However as noted above the volume saved can be used to reduce the initial pressure and thus achieve a lower final pressure than would be the case with hydrogen dilution. As a practical matter it will usually be safer and less costly to add more diluent and maintain or even increase the initial fill pressure. From Fig1c it can be seen that a much lower temperature of  $200^\circ\text{C}$  is easily obtained at the cost of less than 10% of the volume being occupied by diluent even at a 10 atm. initial fill pressure and the final pressure would be 31 atm in the very unlikely event of all the germane reacting.

In order to utilize this heat capacity to prevent a fire or an explosion it is necessary to prevent the incipient reaction from heating up neighboring material to the temperature at which it will react and generate heat. This temperature is termed the decomposition temperature for the gas and is determined experimentally as it is specific to the gas. For example Tamaru determines that germane starts to decompose at

278°C. This is the temperature at which the rate of reaction, which is determined by the activation energy of the reaction, becomes perceptible. For silane the initial decomposition begins at 340°C. Thus the prior art assumption that matching the conditions for silane will make handling the hydride as safe as it is for silane is not really valid. This is particularly the case if the hydride to be matched to silane preferably decomposes heterogeneously in contrast to the homogeneous decomposition of silane. For hydrides there may be a homogeneous reaction, which occurs in the vapor phase, and a heterogeneous reaction, which occurs on the surface. A gaseous diluent is inherently effective at absorbing heat from a homogeneous reaction since it is evenly spread throughout the volume by virtue of diffusion and it adsorbs heat because of its heat capacity but does not contribute heat because it does not react. The solid diluent is inherently effective at absorbing heat from a heterogeneous reaction since the reaction occurs on the surface of the solid diluent and it adsorbs heat because of its heat capacity but does not contribute heat because it does not react. For many unstable hydrides, as shown by Devyatikh in Table 4, the heterogeneous reaction has the lower activation energy and is thus more likely to occur. Thus for a gaseous diluent such as hydrogen the hot spot occurs on the surface but the hydrogen is mixed in with the hydride gas and must move to the surface to cool it. This movement will also bring fresh reactant to the hot spot. In contrast if the heat of the initial reaction is removed directly by the solid diluent it is feasible to prevent the creation of a hot spot which could bring fresh supplies of reactant to the incipient reaction by virtue of natural convection. Thus the total volume of the enclosure must be subdivided into smaller volumes so that the heat from the incipient reaction in one volume cannot spread to neighboring volumes, but is instead absorbed in heating the solid diluent, and to slow the flow of reactant to the incipient reaction site.

1 In order to accomplish this important function of the invention, there is shown in Fig. 2a  
2 a gas cylinder with two different means of providing the subdivided volumes within the  
3 gas cylinder. The gas cylinder consists of a main body 1, which stores the bulk of the  
4 gas and a smaller diameter neck 2, where the cylinder valve is attached. The body of  
5 the cylinder is filled with packing 3, which can be poured in through the smaller diameter  
6 neck. The neck itself is filled with a woven aluminum pad of the same diameter as the  
7 inside of the neck. The poured packing is poured in slowly and vibrated to prevent  
8 formation of voids and to avoid headspace at the top of the main body.

9 The woven pad is further compressed during the installation of the valve as it is  
10 screwed into the neck, which provides pressure on the poured packing as a way of  
11 compensating for movement of the packing that might cause voids to appear. It should  
12 be noted that the main body 1 of the cylinder does provide some solid diluent effect but  
13 it is not as effective or reliable as the packing or mesh because it does not subdivide the  
14 volume. It can be seen that if the diameter of the main body becomes smaller the  
15 effectiveness of the diluent effect of the main body will grow as the surface area capable  
16 of absorbing heat grow relative to the volume capable of generating the heat.

17 In fig 2b there is shown a horizontal pipe 1, with walls 2, and a fiber filling that is the  
18 same diameter as the internal diameter of the pipe. This avoids the problem of settling  
19 of the packing material which might provide an undivided head space wherein a  
20 reaction might propagate. The fiber is retained in the pipe section with a porous or  
21 perforated retention plate, 4, at each end to prevent pressure surges from dislodging the  
22 fiber. The fiber could be glass, steel, stainless steel or aluminum wool or could be a  
23 mesh or series of perforated plates. In accordance with the present invention, Figure 3  
24 is a schematic diagram which shows how the various elements of a packed distillation  
25 column, Fig. 3a, typical of the prior art, would be converted to be safe to operate for the

1 production of concentrated unstable hydrides as shown in Fig 3 b. In Fig 3a the feed  
2 pipe 1, the overhead line 2 and the bottom line 3, are shown as bare pipes. The feed to  
3 the column enters through a distributor 6, into the empty center 7, of the column. Above  
4 the center is the packed rectifying section 4, then the empty top of the column, 8, within  
5 which is the condenser coil 9. Below the center is the packed stripping section 5, and the  
6 empty bottom of the column 10 within which is the reboiler coil 10. In the conversion to  
7 a safe system each of these empty areas, 1, 2, 3, 6, 7, 8 & 10 must be subdivided and  
8 provided with a widely distributed solid diluent. The two packed sections, 4 & 5, are  
9 already subdivided and may provide adequate dilution but must be analyzed to ensure  
10 that there is adequate heat capacity in the solid diluent under the normal operating  
11 conditions to prevent a temperature rise from the operating temperature to the  
12 decomposition temperature in the event of an incipient fire or explosion. The open  
13 pipes and column sections must be filled with solid diluent to subdivide these  
14 enclosures and provide heat capacity. As is shown in Fig. 3b the inlet, 21, and outlet,  
15 pipes, 22 & 23, are filled with a mesh pad and the bottom, 30, center, 27, and top, 28,  
16 sections of the column are filled with poured packing. The column packing in the rectifier  
17 section, 24 and stripper section, 25, is left unchanged. The distributor 26 is filled with  
18 fibrous packing. It is known that there are many different ways of arranging a  
19 distillation column or other separation device but one knowledgeable in the art should  
20 be able to make any design safe by subdividing any open space with a solid diluent  
21 selected and sized to prevent an incipient reaction from raising the temperature from the  
22 system operating temperature to the decomposition temperature. The use of the  
23 system operating temperature as the base point for the design is required. Use of  
24 refrigeration will be beneficial in reducing the diluent requirements but standard process  
25 safety management techniques should be followed to ensure that unsafe conditions

1 couldn't occur due to inadvertent warm-up of the system. Certain distillation designs  
2 may not function well when subdivided and hence these designs cannot be used. For  
3 example a trayed distillation column has spaces between each tray and filling these  
4 spaces may interfere with the tray action and is therefore not feasible.

5 To accomplish the important function of the invention of using a poured packing  
6 to subdivide the enclosure and provide the heat capacity needed for the solid diluent,  
7 there is shown in Fig. 4 a simple design to show the required characteristics and the  
8 effects of randomness in the packing process. Fig. 4a shows an aluminum tube 1, of  
9 0.5" outside diameter and 0.028" thickness cut into 1" lengths. Fig. 4b shows that when  
10 these tubes are loosely stacked there is also an outside space, which corresponds to  
11 the area of the square circumscribed on the outside diameter minus the cross-sectional  
12 area of the tube. Thus the volume of aluminum is 0.0415 cu inches and the total  
13 volume is 0.25 cu inches, which corresponds to 16.6% aluminum. Fig 4c shows the  
14 most compact packing possible. The actual packing achieved in random packing will be  
15 between these two extremes. Designing for the loosest packing will ensure that the  
16 loosest sub volume still meet the requirements. The tighter packed areas will have a  
17 bigger safety margin. As a practical matter it is required that a minimum weight of  
18 packing be installed to obtain the desired peak temperature rise and that there be few if  
19 any large voids or a headspace. Thus by knowing the weight of the packing and the  
20 volume of the enclosure it is possible to know if it has been well packed and by  
21 observation it can be seen if there is any headspace and additional material can be  
22 added to fill it. For further assurance it is feasible to apply a safety factor by increasing  
23 the volume of aluminum. It is also feasible to perform detailed finite element analysis  
24 calculations on the temperature distribution and heat production with time for a given  
25 packing geometry as done by Lund et al. This will enable the calculation of the heat

1 loss from the immediate area of the incipient reaction and thus spread the heat  
2 absorption over a greater volume of diluent and gas that absorb the heat generated,  
3 which reduces the temperature rise. This is also the case for the hydrogen diluent as a  
4 greater volume of gas is heated than the core gas, which is heated to the decomposition  
5 temperature. This accounts for the success of the prior art in diluting germane to 20%,  
6 which results in a calculated peak temperature of 463° C when Tamaru reports the  
7 minimum decomposition temperature of germane is 278°C. Such calculations are  
8 particularly appropriate for germane and other unstable hydrides because the  
9 heterogeneous reaction on the surface has a smaller activation energy than the  
10 homogeneous reactions hence most incipient reactions will occur on the surface where  
11 the heat can be removed by conduction.

12 Many other pourable diluent designs are also possible and it is also possible to  
13 use commercially available column packings but these are primarily designed for gas  
14 liquid contacting which is not required for solid diluent. For situations requiring very high  
15 diluent volumes it is feasible to use solid balls or granular material such as aluminum  
16 shot or sand. Use of fine materials brings the risk of blowing out the bed so some  
17 retention device may be needed. Such solid materials would have a volume of about  
18 65% based on a typical void fraction of 35%. It is also possible to use wools such as  
19 glass, steel, stainless steel, copper or aluminum wools, which have low, bulk density  
20 and come in different grades. Use of plastics is feasible in a reusable way if the melting  
21 point of the plastic is greater than the peak temperature. Use of plastics in a disposable  
22 manner is feasible if the design includes provision for melting of the plastic as a means  
23 to absorb heat.

24 Thus it can be seen that it is feasible to construct safe apparatus for the  
25 production, purification, storage or transportation of unstable hydrides in many different

1 ways by following the method of calculating the required solid diluent to prevent the  
2 peak temperature exceeding the decomposition temperature of the hydride and  
3 subdividing the enclosure volume with the aforementioned solid diluent.

4 While the invention has been described in connection with a preferred  
5 embodiment, it is not intended to limit the scope of the invention to the particular form  
6 set forth, but on the contrary, it is intended to cover such alternatives, modifications,  
7 and equivalents as may be included within the spirit and scope of the invention as  
8 defined by the appended claims.